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(54) **Process for deposition of oxides and nitrides with compositional gradients**

Verfahren zur Abscheidung von Oxyden und Nitriden mit Zusammensetzungsgradienten

Procédé de dépôt des oxydes et nitrures à gradients de composition

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• **JONG-HWANG YOON ET AL: "STABILITY OF  
UNDOPED HYDROGENATED AMORPHOUS  
SILICON MULTILAYER FILMGROWN WITH  
ALTERNATING SUBSTRATE TEMPERATURE"  
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**Description****CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** Not applicable.

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

**[0002]** Not applicable

**BACKGROUND OF THE INVENTION**

**[0003]** Multicomponent metal containing materials, such as mixed-metal/metalloid oxides and nitrides often have unique physical properties that each individual metal/metalloid oxide/nitride component does not possess. For example, some mixed metal oxides can be used for high dielectric constant materials, R. Cava et al., *Nature*, vol. 377, p.215, (1995), ferroelectrics, L. M. Sheppard, *Ceramic Bulletin*, vol.71, p.85, (1992), high temperature superconductors, D. L. Schulz et al. *Adv. Mater.*, vol.6, p.719, (1994), catalysts, M. Gugliemi et al., *J. Electrochem. Soc.*, vol.139, p.1655, (1992), and corrosion resistant coating, N. Hara et al., *J. Electrochem. Soc.*, vol. 146, p.510, (1999). Also some mixed metal nitrides show good diffusion barrier properties, X. Sun et al., *J. Appl. Phys.* Vol.81, p.664, (1997), superconducting, R. B. Van Dover, *Chem. Mater.*, vol. 5, p.32, (1993), and magnetic properties, K. Schunitzke et al., *Appl. Phys. Lett.*, vol. 57, p. 2853, (1990).

**[0004]** As the size of integrated circuits (IC) devices becomes aggressively smaller, thin films deposited by chemical vapor deposition (CVD) demonstrates an advantage over physical vapor deposition (PVD) methods in terms of conformal coverage on various non-planar surfaces. In general, liquid precursors are preferred for CVD applications due to the ease and reproducibility in precursor delivery.

**[0005]** Common precursor delivery methods used in CVD processing include vapor draw, bubbling with carrier gas, mist droplet (aerosol) delivery, and direct liquid injection (DLI). DLI is particularly a preferred method for the consistent delivery of multi-components because it delivers the same ratio of constituents to the reactor as are in the source container. DLI has the added advantage of storing the precursor at room temperature and heating only the amount required to be delivered, and therefore, improving precursor shelf life.

**[0006]** Metal silicates for electronic materials have been studied by those skilled in the art. For instance, Wilk, et. al., Hafnium and Zirconium silicates for advanced gate dielectrics, *Journal of Applied Physics*, Vol. 87, No. 1, 2000, pp. 484-492 describe the use of metal silicates as gate dielectric films with varying metal contents. Depositions were by sputtering and e-beam evaporation. Separate films were deposited at specific temperatures chosen over the range of 25°C to 600°C.

Kolawa, et. al., Amorphous Ta-Si-N thin-film alloys as diffusion barrier in Al/Si metallizations, *J. Vac. Sci. Technol. A* 8 (3), May/June 1990, pp. 3006-3010, indicates that Ta-Si-N films of a wide range of compositions were prepared by rf reactive sputtering. The films were used as diffusion barriers. Nitrogen incorporation was varied by varying the amount of nitrogen in the reaction atmosphere. Sun, et. al., Reactively sputtered Ti-Si-N films. II. Diffusion barriers for Al and Cu metallizations on Si, *J. Appl. Phys.* 81 (2) 15 Jan. 1997, pp. 664-671, describes sputtered films of Ti-Si-N for interfacing with Al and Cu. Nitrogen content was varied during the depositions. Wilk, et. al., Electrical properties of hafnium silicate gate dielectrics deposited directly on silicon, *Applied Physics Letters*, Vol. 74, No. 19, 10 May 1999, pp. 2854-2856, describes  $\text{HfSi}_x\text{O}_y$  gate dielectric films. Films were deposited at 500°C.

**[0007]** Other mixed metal systems of general interest are; VanDover, et. al., Discovery of a useful thin-film dielectric using a composition-spread approach, *Nature*, Vol. 392, 12 March 1998, pp. 162-164, discloses capacitance devices with high dielectric films of Zr-Sn-Ti-O. Depositions were performed below 300°C; VanDover, et. al., Deposition of Uniform Zr-Sn-Ti-O Films by On-Axis Reactive Sputtering, *IEEE Electron Device Letters*, Vol. 19, No. 9, Sept. 1998, pp. 329-331, describes sputtering at 200°C  $\pm$  10°C; Cava, et. al., enhancement of the dielectric constant of  $\text{Ta}_2\text{O}_5$  through Substitution with  $\text{TiO}_2$ , *Nature*, Vol. 377, 21 Sept. 1995, pp. 215-217, prepared ceramic samples of  $\text{Ta}_2\text{O}_5$ - $\text{TiO}_2$  by physically mixing and firing at temperatures of 1350-1400°C; Cava, et. al., Dielectric properties of  $\text{Ta}_2\text{O}_5$ - $\text{ZrO}_2$  polycrystalline ceramics, *J. Appl. Phys.* 83, (3), 1 Feb. 1998, pp. 1613-1616, synthesized ceramics by physical mixture and firing; US Patents 5,923,056 and 5,923,524 address mixed metal oxides for electronic materials.

**[0008]** In the field of electronic materials for device fabrication, such as interlayer dielectrics, gate oxides, capacitors and barrier layers, it is desirable to have materials which have a varying compositional gradient of mixed metals or metal/metalloid composition in either oxide, oxynitride or nitride form. The prior art has failed to provide a quick, simple and reproducible method for controllably producing a deposited layer of mixed metal/metalloid oxides, oxynitride or nitrides having a compositional gradient over the depth of the deposited layer.

**[0009]** The present invention overcomes this deficiency as will be set forth in greater detail below.

**BRIEF SUMMARY OF THE INVENTION**

**[0010]** A process for deposition of a multiple metal and metalloid compound layer with a compositional gradient of the metal and metalloid in the layer on a substrate of an electronic material, comprising: a) providing two or more metal-ligand and metalloid-ligand complex precursors which preferably constitute a liquid at ambient conditions whereby the metal is selected from the group con-

sisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, and the metalloid is selected from the group consisting of boron, silicon, arsenic, tellurium and mixtures thereof and the ligand is selected from the group consisting of alkyls, alkoxides, oxygen and nitrogen substituted analogs; b) delivering the mixture to a deposition zone where the substrate is located; c) contacting the substrate under deposition conditions with the precursors, where the contacting the substrate under deposition conditions is preferably selected from the group consisting of chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition; d) varying the temperature of the deposition conditions from a first temperature to a second distinct temperature which is at least 40°C from said first temperature during the contact, and e) depositing a multiple metal and metalloid compound layer on the substrate from the precursors resulting in the compositional gradient of the metal and metalloid in the layer as a result of step d); wherein said mixture is mixed with a source of oxygen or nitrogen prior to depositing said multiple metal compound layer on said substrate. An oxygen source can be added to result in a metal-metalloid oxide, or a nitrogen source can be added to result in a metal-metalloid nitride, and a mixture of oxygen source and nitrogen source can be added to result in a metal-metalloid oxynitride. The metalloid would preferably be silicon.

#### BRIEF DESCRIPTION OF THE DRAWING

**[0011]** The drawing is a graph of atomic percent concentration and dielectric constant charted against temperature of a preferred embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0012]** In the present invention a new metal and metalloid deposition resulting in a compositional gradient is disclosed that can be used for precursor dispersing delivery methods, including DLI in CVD applications. Preferably, the precursors are a solventless mixture.

**[0013]** The volatile components are chosen such that:

- 1) They are chemically compatible, therefore, no non-volatile polymeric or multinuclear species are formed.
- 2) No precipitates are generated due to ligand exchange on the metals or inter ligand reactions.
- 3) The mixtures maintain low viscosity and thermal stability.
- 4) Undesired redox chemistry will not take place (eg.  $M^{+1} + M^{+3} \rightarrow M^{+2} + M^{+2}$ ).

**[0014]** In the preferred form, liquid mixtures can be prepared either by directly mixing liquid metal/metalloid complexes or dissolving solid metal or metalloid complex(es)

in liquid metal or metalloid complex(es). In these systems, no solvent is needed to dissolve or dilute the precursor mixtures to achieve a total liquid phase of the resulting mixtures. The preferred non-solvent containing precursor mixtures lower the burden of abatement of the CVD effluent in the exhaust, because there is no extra volatile organic medium to be collected after the CVD processing. Besides, since no solvent is used in the preferred liquid mixtures described herein, high throughput of metal containing vapor can be delivered into the CVD reactor. Thus, the overall CVD process using these preferred liquid precursor mixtures is more environmentally benign and cost effective than liquid injection delivery of precursor solutions. The multi-component precursors used in the present invention are preferably water-like low viscosity materials at room temperature and have sufficient volatility at a relatively low temperature and can be easily delivered into a CVD system. It is also possible to practice the present invention using traditional mixtures of precursors in an appropriate solvent.

**[0015]** Surprisingly, in the present invention, as exemplified by the case of  $Zr_x-Si_y-O_z$  CVD from a mixture of  $Zr(NEt_2)_4$  and  $Si(NMe_2)_4$ , an unexpected dependency of the film composition on deposition temperature was observed. The results show that metal silicate thin films with metal/metalloid compositional gradient are deposited by controllably varying the deposition temperatures. The gate dielectric films with compositional gradients, such as, a silicon rich layer toward the silicon substrate vs a metal rich layer toward the gate metal may show unique compatibility and performance advantage in IC device fabrication. Metal silicate thin films whose refractivity gradients controlled by the silicon/metal compositional gradients may also be useful for electro-optics applications.

**[0016]** In the preferred mode, the mixture of two or more metal-ligand and metalloid-ligand complex precursors, which preferably constitute a liquid at ambient conditions, have ligands which can be the same or different and are selected from the group consisting of alkyls, alkoxides, oxygen and nitrogen substituted analogs.

**[0017]** Appropriate choice of precursors, in the presence of oxidant or nitrogen containing reactant, would provide either mixed metal/metalloid oxides, nitrides, and oxynitrides. In addition, using proper precursor mixtures and CVD conditions, it is also possible to grow mixed metal/metalloid alloys, carbides, carbonitrides, oxycarbonitrides, sulfides, phosphides, borides, arsenides, antimonides, selenides, tellurides, and mixtures thereof.

**[0018]** In addition to thermal low pressure CVD, the above precursors could be used for atmospheric pressure CVD, sub-atmospheric pressure CVD, plasma, photo, radical, or laser enhanced CVD deposition, and jet vapor deposition well recognized deposition techniques, or by atomic layer deposition. In atomic layer deposition, an approximately single layer of precursor molecules are adsorbed on a surface. A second reactant is dosed onto the first precursor layer followed by a reaction between the second reactant and the first reactant already on the

surface. This alternating procedure is repeated to provide the desired thickness of element or compound in a near atomic thickness layer.

**[0019]** Furthermore, appropriate choice of mixture precursors may also be applied to sol-gel processing and spin coating of films.

**[0020]** The ambient conditions are preferably less than or equal to 200°C, more preferably less than or equal to 40°C, and less than or equal to 2.07 bar (30 psig).

**[0021]** The first temperature is in the range of 200-350°C and the second distinct temperature is at least 40°C above said first temperature, preferably 300-450°C or above, to obtain the compositional gradient of the resulting film desired. It is preferable to vary the temperature during deposition in a constant manner from the low starting temperature to the high ending temperature. However, it is appreciated that the temperature can be manipulated to achieve any compositional gradient desired for a given metal/metalloid system and the desired compositional gradient.

**[0022]** The mixture is mixed with a source of oxygen prior to depositing the multiple metal/metalloid compound layer on the substrate to form the metal and metalloid oxide. The source of oxygen can be selected from the group consisting of oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, air and mixtures thereof. Alternatively, the mixture is mixed with a source of nitrogen prior to depositing the multiple metal/metalloid compound layer on the substrate to form the metal and metalloid nitride. The source of nitrogen can be selected from the group consisting of nitrogen, ammonia, hydrazine, alkylhydrazine, hydrogen azide, alkylamine and mixtures thereof. Sources of nitrogen and oxygen or ligands with those elements can be used to produce mixed metal and metalloid oxynitrides.

**[0023]** The multiple metal and metalloid compound layer is selected from the group consisting of mixed metal and metalloid alloys, mixed metal and metalloid oxides, mixed metal metalloid nitrides, mixed metal and metalloid carbides, mixed metal and metalloid carbonitrides, mixed metal and metalloid oxycarbonitrides, mixed metal and metalloid oxycarbides, mixed metal and metalloid oxynitrides, mixed metal and metalloid sulfides, mixed metal and metalloid phosphides, mixed metal and metalloid borides, mixed metal and metalloid arsenides, mixed metal and metalloid antimonides, mixed metal and metalloid selenides, mixed metal and metalloid tellurides and mixtures thereof.

**[0024]** The metalloid is selected from the group consisting of boron, silicon, arsenic, tellurium, and mixtures thereof. Preferably, the metalloid is silicon.

**[0025]** The metal is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, and mixtures thereof.

**[0026]** The present invention will now be illustrated in several nonlimiting examples.

#### Example 1: CVD of Zr-Si-O thin films from $Zr(NEt_2)_4$ and $Si(NMe_2)_4$

**[0027]** A solventless mixture of  $Zr[N(CH_2CH_3)_2]_4$  and  $Si[N(CH_3)_2]_4$ , (molar ratio Zr:Si = 1:1) metal-ligand complex precursors was delivered at 0.12ml per minute to a direct liquid injection system with a vaporization temperature of 110°C using a helium sweep gas of 100sccm with a variable oxygen flow, onto a wafer substrate target for mixed metal compound film deposition where the wafer was held between 280 and 430°C. The reactor chamber pressure was 1.33 mbar (1Torr). Up to 380°C, the deposition rate increased from 450 to 560 angstroms per minute on bare silicon with oxygen flows of 150sccm as the deposition temperature increases. At the deposition temperatures 400°C and 430°C, the deposition rates dropped to 360 angstroms per minute then to 150 angstroms per minute, respectively. The attached drawing shows the X-ray photoelectron spectroscopy analysis of film compositions vs deposition temperatures. At deposition temperatures below 380°C, zirconium was predominantly incorporated in the film while the ratio of silicon incorporation increased at higher deposition temperatures. Also shown in the drawing are the dielectric constants of the as-deposited films determined by capacitance-voltage measurement which demonstrated that the dielectric constants of the films ranged from 5 to 13 depending on the metal composition. The refractive indexes of the films deposited at 280-380°C were 1.96-2.02. The films deposited at 400-430°C had lower refractive indices of 1.70-1.62. Refractive indexes decreased as the silicon content increases with higher deposition temperatures.

#### Example 2: CVD of Zr-Si-N thin films from $Zr(NEt_2)_4$ and $Si(NMe_2)_4$

**[0028]** A solventless mixture of  $Zr[N(CH_2CH_3)_2]_4$  and  $Si[N(CH_3)_2]_4$ , (molar ratio Zr:Si = 1:1) metal-ligand complex precursors was delivered at 0.12ml per minute to a direct liquid injection system with a vaporization temperature of 90°C using a helium sweep gas of 100sccm with an ammonia flow of 200sccm, onto a wafer substrate target for mixed metal compound film deposition where the wafer was held between 300 and 360°C. The deposition rate ranged from 285 to 320 angstroms per minute on bare silicon. The reactor chamber pressure was 1.33 mbar (1Torr).

#### Example 3: CVD of Ta-Si-O thin films from t-BuN=Ta( $NEt_2$ )<sub>3</sub> and $Si(NMe_2)_4$

**[0029]** A solventless mixture of t-BuN=Ta( $N(CH_2CH_3)_2$ )<sub>3</sub> and  $Si[N(CH_3)_2]_4$ , (molar ratio Ta:Si = 2.5:1) metal-ligand complex precursors was delivered at 0.1ml per minute to a direct liquid injection system with a vaporization temperature of 100°C using a helium sweep gas of 200sccm with variable flows of 50 to

150sccm oxygen, onto a wafer substrate target for mixed metal compound film deposition where the wafer was held between 300 and 435°C. The reactor chamber pressure was 1.33 mbar (1Torr). The activation energy of the deposition was 29kcal/mol.

**Example 4: CVD of Ta-Si-N thin films from t-BuN=Ta(NEt<sub>2</sub>)<sub>3</sub> and Si(NMe<sub>2</sub>)<sub>4</sub>**

**[0030]** A solventless mixture of t-BuN=Ta[N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, (molar ratio Ta:Si = 2.5:1) metal-ligand complex precursors was delivered at 0.1ml per minute to a direct liquid injection system with a vaporization temperature of 100°C using a helium sweep gas of 200sccm with an ammonia flow of 73sccm, onto a wafer substrate target for mixed metal compound film deposition where the wafer was held between 310 and 350°C. The reactor chamber pressure was 1.33 mbar (1Torr). The activation energy of the deposition was 34 kcal/mol.

**[0031]** The prior art has failed to provide a method for depositing mixed metal/metalloid oxides and nitrides as electronic layers or devices in semiconductor materials where the metal/metalloid compositional gradient is varied by the temperature of the deposition process. The present invention overcomes this deficiency in the prior art with a simple, efficient reproducible process for varying metal/metalloid oxide, oxynitride or nitride materials compositional gradients over the deposition process by the controlled deposition temperature to provide unique deposition products with varying electrical properties useful in the electronic materials fabrication industry.

**[0032]** The present invention has been set forth with regard to several specific embodiments, but the full scope of the present invention should be ascertained from the claims which follow.

## Claims

1. A process for deposition of a multiple metal and metalloid compound layer with a compositional gradient of the metal and metalloid of the layer on a substrate of an electronic material, comprising:
  - a) providing a mixture of two or more metal-ligand and metalloid-ligand complex precursors; whereby the metal is selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, and the metalloid is selected from the group consisting of boron, silicon, arsenic, tellurium and mixtures thereof and the ligand is selected from the group consisting of alkyls, alkoxides, oxygen and nitrogen substituted analogs;
  - b) delivering said metal-ligand and metalloid-ligand complex precursors to a deposition zone where said substrate is located;
  - c) contacting said substrate under deposition conditions with said metal-ligand and metalloid-ligand complex precursors;
  - d) varying the temperature of said deposition conditions from a first temperature to a second distinct temperature which is at least 40°C from said first temperature during said contact, and
  - e) depositing a multiple metal and metalloid compound layer on said substrate from said metal-ligand and metalloid-ligand complex precursors resulting in said compositional gradient of the metal and metalloid in said layer as a result of step d);
- wherein said mixture is mixed with a source of oxygen or nitrogen prior to depositing said multiple metal compound layer on said substrate.
2. A process of claim 1, wherein said contacting said substrate under deposition conditions in step c) is selected from the group consisting of chemical vapor deposition, spray pyrolysis, jet vapor deposition, sol-gel processing, spin coating, chemical solution deposition, and atomic layer deposition.
3. A process of claim 1, wherein two or more metal-ligand and metalloid-ligand complex precursors which constitute a liquid at ambient conditions are provided as a solventless mixture in step a); said solventless mixture is delivered by direct liquid injection to a flash vaporization zone to vaporize said solventless mixture in step b); said substrate is contacted under deposition conditions with a resulting vapor of said solventless mixture in step c).
4. The process of anyone of claims 1 to 3 wherein said source of oxygen is selected from the group consisting of oxygen, ozone, nitrous oxide, nitric oxide, nitrogen dioxide, water, hydrogen peroxide, air and mixtures thereof.
5. The process of anyone of claims 1 to 3 wherein said source of nitrogen is selected from the group consisting of nitrogen, ammonia, hydrazine, alkylhydrazine, hydrogen azide, alkylamine and mixtures thereof.
6. The process of anyone of claims 1 to 5 wherein said multiple metal and metalloid compound layer is selected from the group consisting of mixed metal and metalloid alloys, mixed metal and metalloid oxides, mixed metal and metalloid nitrides, mixed metal and metalloid carbides, mixed metal and metalloid carbonitrides, mixed metal and metalloid oxycarbonitrides, mixed metal and metalloid oxycarbides, mixed metal and metalloid oxynitrides, mixed metal and metalloid borides mixed metal and metalloid

sulfides, mixed metal and metalloid phosphides, mixed metal and metalloid arsenides, mixed metal and metalloid antimonides, mixed metal and metalloid selenides, mixed metal and metalloid tellurides and mixtures thereof.

7. The process of anyone of claims 1 to 6 wherein said metalloid is silicon. 5
8. The process of anyone of claims 1 to 7 wherein said first temperature is in the range of 200-350 °C and said second distinct temperature is at least 40 °C above said first temperature. 10
9. The process of Claim 3 wherein said ambient conditions are less than or equal to 200 °C and less than or equal to 2.07 bar (30 psig). 15
10. The process of anyone of claims 1 to 9 wherein said metal-ligand complex precursor is  $Zr[N(CH_2CH_3)_2]_4$ , said metalloid-ligand complex precursor is  $Si[N(CH_3)_2]_4$ , said first temperature is 280 °C and said second distinct temperature is 430 °C. 20
11. The process of anyone of claims 1 to 9 wherein said mixture is mixed with a source of oxygen prior to depositing said multiple metal compound layer on said substrate wherein said metal-ligand complex precursor is  $t\text{-butylN}=\text{Ta}[N(CH_2CH_3)_2]_3$ , said metalloid-ligand complex precursor is  $Si[N(CH_3)_2]_4$ , said first temperature is 300 °C and said second distinct temperature is 435 °C. 25 30
12. The process of anyone of claims 1 to 9 wherein said mixture is mixed with a source of nitrogen prior to depositing said multiple metal compound layer on said substrate wherein said metal-ligand complex precursor is  $Zr[N(CH_2CH_3)_2]_4$ , said metalloid-ligand complex precursor is  $Si[N(CH_3)_2]_4$ , said first temperature is 300 °C and said second distinct temperature is 360 °C. 35 40
13. The process of anyone of claim 1 to 10 wherein said mixture is mixed with a source of nitrogen prior to depositing said multiple metal compound layer on said substrate wherein said metal-ligand complex precursor is  $t\text{-butylN}=\text{Ta}[N(CH_2CH_3)_2]_3$ , said metalloid-ligand complex precursor is  $Si[N(CH_3)_2]_4$ , said first temperature is 310 °C and said second distinct temperature is 350 °C. 45 50

#### Patentansprüche

1. Verfahren zur Abscheidung einer multiplen Metall- und Metalloidverbindungsschicht mit einem Zusammensetzungsgradienten des Metalls und Metalloids der Schicht auf einem Substrat eines elektronischen 55

Materials, umfassend:

- a) Bereitstellen eines Gemischs aus zwei oder mehr Metall-Ligand- und Metalloid-Ligand-Komplexvorläufern, wobei das Metall ausgewählt wird aus der Gruppe, bestehend aus Titan, Zirkonium, Hafnium, Vanadium, Niob und Tantal, und das Metalloid ausgewählt wird aus der Gruppe, bestehend aus Bor, Silicium, Arsen, Tellur und deren Gemischen und der Ligand ausgewählt wird aus der Gruppe, bestehend aus Alkylen, Alkoxiden sowie mit Sauerstoff und Stickstoff substituierten Analogenen;
- b) Einleiten dieser Metall-Ligand- und Metalloid-Ligand-Komplexvorläufer in eine Abscheidezone, wo sich das Substrat befindet;
- c) In-Kontakt-Bringen des Substrats unter Abscheidebedingungen mit den Metall-Ligand- und Metalloid-Ligand-Komplexvorläufern;
- d) Verändern der Temperatur der Abscheidebedingungen von einer ersten Temperatur auf eine zweite unterschiedliche Temperatur, die sich während des Kontakts um mindestens 40 °C von der ersten Temperatur unterscheidet; und
- e) Abscheiden einer multiplen Metall- und Metalloidverbindungsschicht auf das Substrat aus den Metall-Ligand- und Metalloid-Ligand-Komplexvorläufern, was zu dem Zusammensetzungsgradienten des Metalls und Metalloids in der Schicht als Ergebnis von Schritt d) führt;

wobei das Gemisch vor dem Abscheiden der multiplen Metallverbindungsschicht auf das Substrat mit einer Sauerstoff- oder Stickstoffquelle gemischt wird.

2. Verfahren nach Anspruch 1, bei dem das In-Kontakt-Bringen des Substrats unter Abscheidebedingungen in Schritt c) ausgewählt wird aus der Gruppe, bestehend aus chemischer Dampfabscheidung, Sprühpolymerisation, Dampfstrahlabscheidung, Sol-Gel-Verarbeitung, Spinbeschichtung, Abscheidung einer chemischen Lösung und Abscheidung einer Atomschicht.
3. Verfahren nach Anspruch 1, bei dem zwei oder mehrere Metall-Ligand- und Metalloid-Ligand-Komplexvorläufer, die bei Umgebungsbedingungen eine Flüssigkeit bilden, in Schritt a) als lösungsmittelfreies Gemisch zur Verfügung gestellt werden; wobei das lösungsmittelfreie Gemisch durch direktes flüssiges Einspritzen in eine Flash-Verdampfungszone zugeführt wird, um das lösungsmittelfreie Gemisch in Schritt b) zu verdampfen; wobei das Substrat in Schritt c) unter Abscheidebedingungen mit dem resultierenden Dampf aus dem lösungsmittelfreien Gemisch in Kontakt gebracht wird.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die Sauerstoffquelle ausgewählt wird aus der Gruppe, bestehend aus Sauerstoff, Ozon, Distickoxid, Stickoxid, Stickstoffdioxid, Wasser, Wasserstoffperoxid, Luft und deren Gemischen. 5
5. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die Stickstoffquelle ausgewählt wird aus der Gruppe, bestehend aus Stickstoff, Ammoniak, Hydrazin, Alkylhydrazin, Hydrogenazid, Alkylamin und deren Gemischen. 10
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem die multiple Metall- und Metalloidverbindingsschicht ausgewählt wird aus der Gruppe, bestehend aus gemischten Metall- und Metalloidlegierungen, gemischten Metall- und Metalloiddoxiden, gemischten Metall- und Metalloiddinitriden, gemischten Metall- und Metalloiddcarbiden, gemischten Metall- und Metalloiddcarbonitriden, gemischten Metall- und Metalloiddoxycarbonitriden, gemischten Metall- und Metalloiddoxycarbiden, gemischten Metall- und Metalloiddoxynitriden, gemischten Metall- und Metalloiddboriden, gemischten Metall- und Metalloiddsulfiden, gemischten Metall- und Metalloiddphosphiden, gemischten Metall- und Metalloiddarseniden, gemischten Metall- und Metalloiddantimoniden, gemischten Metall- und Metalloiddseleniden, gemischten Metall- und Metalloiddtelluriden und deren Gemischen. 15  
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7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Metalloid Silicium ist. 30
8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die erste Temperatur im Bereich von 200 bis 350°C liegt und die zweite unterschiedliche Temperatur um mindestens 40°C über der ersten Temperatur liegt. 35
9. Verfahren nach Anspruch 3, bei dem die Umgebungsbedingungen 200°C oder weniger und 2,07 bar (30 psig) oder weniger betragen. 40
10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem der Metall-Ligand-Komplexvorläufer  $Zr[N(CH_2CH_3)_2]_4$  ist, der Metalloid-Ligand-Komplexvorläufer  $Si[N(CH_3)_2]_4$  ist, die erste Temperatur 280°C beträgt und die zweite unterschiedliche Temperatur 430°C beträgt. 45  
50
11. Verfahren nach einem der Ansprüche 1 bis 9, bei dem das Gemisch vor dem Abscheiden der multiplen Metallverbindingsschicht auf das Substrat mit einer Sauerstoffquelle gemischt wird und wobei der Metall-Ligand-Komplexvorläufer  $t\text{-Butyl-N-Ta}[N(CH_2CH_3)_2]_3$  ist, der Metalloid-Ligand-Komplexvorläufer  $Si[N(CH_3)_2]_4$  ist, die erste Temperatur 300°C beträgt und die zweite unterschiedliche Temperatur 435°C beträgt. 55
12. Verfahren nach einem der Ansprüche 1 bis 9, bei dem das Gemisch vor dem Abscheiden der multiplen Metallverbindingsschicht auf das Substrat mit einer Stickstoffquelle gemischt wird und wobei der Metall-Ligand-Komplexvorläufer  $Zr[N(CH_2CH_3)_2]_4$  ist, der Metalloid-Ligand-Komplexvorläufer  $Si[N(CH_3)_2]_4$  ist, die erste Temperatur 300°C beträgt und die zweite unterschiedliche Temperatur 360°C beträgt.
13. Verfahren nach einem der Ansprüche 1 bis 10, bei dem das Gemisch vor dem Abscheiden der multiplen Metallverbindingsschicht auf das Substrat mit einer Stickstoffquelle gemischt wird und wobei der Metall-Ligand-Komplexvorläufer  $t\text{-Butyl-N-Ta}[N(CH_2CH_3)_2]_3$  ist, der Metalloid-Ligand-Komplexvorläufer  $Si[N(CH_3)_2]_4$  ist, die erste Temperatur 310°C beträgt und die zweite unterschiedliche Temperatur 350°C beträgt.

# Revendications

1. Procédé de dépôt d'une couche de plusieurs composés métalliques et métalloïdes à gradient de composition du métal et du métalloïde de la couche sur un substrat fait d'un matériau électronique, comprenant les étapes consistant à :

- a) fournir un mélange de deux précurseurs de complexes métal-ligand et métalloïde-ligand ou plus ; moyennant quoi le métal est choisi dans le groupe composé par le titane, le zirconium, le hafnium, le vanadium, le niobium, le tantale, et le métalloïde est choisi dans le groupe composé par le bore, le silicium, l'arsenic, le tellure et leurs mélanges et le ligand est choisi dans le groupe composé par les alkyles, les alcoxydes, les analogues substitués par l'oxygène et l'azote ;
- b) apporter lesdits précurseurs de complexes métal-ligand et métalloïde-ligand vers une zone de dépôt où ledit substrat est situé ;
- c) mettre en contact ledit substrat dans des conditions de dépôt avec lesdits précurseurs de complexes métal-ligand et métalloïde-ligand ;
- d) faire varier la température desdites conditions de dépôt depuis une première température jusqu'à une seconde température distincte qui dépasse d'au moins 40°C ladite première température durant ledit contact, et
- e) déposer une couche de plusieurs composés métalliques et métalloïdes sur ledit substrat à partir desdits précurseurs de complexes métal-ligand et métalloïde-ligand aboutissant au dit gradient de composition du métal et métalloïde dans ladite couche suite à l'étape d) ;

- dans lequel ledit mélange est mélangé avec une source d'oxygène ou d'azote avant de déposer ladite couche de plusieurs composés métalliques sur ledit substrat.
2. Procédé selon la revendication 1, dans lequel ladite mise en contact dudit substrat dans des conditions de dépôt à l'étape c) est choisie dans le groupe composé par le dépôt chimique en phase vapeur, la pyrolyse par pulvérisation, le dépôt par évaporation accélérée, le traitement sol-gel, le dépôt par centrifugation, le dépôt chimique en solution et le dépôt par couche atomique.
  3. Procédé selon la revendication 1, dans lequel deux précurseurs de complexes métal-ligand et métalloïde-ligand ou plus qui constituent un liquide à des conditions ambiantes sont fournis sous forme d'un mélange sans solvant à l'étape a) ; ledit mélange sans solvant est apporté par injection directe de liquide vers une zone de vaporisation instantanée pour vaporiser ledit mélange sans solvant à l'étape b) ; ledit substrat est mis en contact dans des conditions de dépôt avec une vapeur résultant dudit mélange sans solvant à l'étape c).
  4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite source d'oxygène est choisie dans le groupe composé par l'oxygène, l'ozone, l'oxyde nitreux, l'oxyde nitrique, le dioxyde d'azote, l'eau, le peroxyde d'hydrogène, l'air et leurs mélanges.
  5. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite source d'azote est choisie dans le groupe composé par l'azote, l'ammoniac, l'hydrazine, l'hydrazine d'alkyle, l'azoture d'hydrogène, l'alkylamine et leurs mélanges.
  6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ladite couche de plusieurs composés métalliques et métalloïdes est choisie dans le groupe composé par des alliages métalliques et métalloïdes mélangés, des oxydes métalliques et métalloïdes mélangés, des nitrures métalliques et métalloïdes mélangés, des carbures métalliques et métalloïdes mélangés, des carbonitrures métalliques et métalloïdes mélangés, des oxycarbonitrures métalliques et métalloïdes mélangés, des oxycarbures métalliques et métalloïdes mélangés, des oxynitrures métalliques et métalloïdes mélangés, des borures métalliques et métalloïdes mélangés, des sulfures métalliques et métalloïdes mélangés, des phosphures métalliques et métalloïdes mélangés, des arséniures métalliques et métalloïdes mélangés, des antimoniures métalliques et métalloïdes mélangés, des sélénures métalliques et métalloïdes mélangés,
- des tellures métalliques et métalloïdes mélangés et leurs mélanges.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit métalloïde est le silicium.
  8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ladite première température est comprise entre 200 et 350°C et ladite seconde température distincte dépasse d'au moins 40°C ladite première température.
  9. Procédé selon la revendication 3, dans lequel lesdites conditions ambiantes sont inférieures ou égales à 200°C et inférieures ou égales à 2,07 bar (30 psig).
  10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel ledit précurseur de complexe métal-ligand est  $Zr[N(CH_2CH_3)_2]_4$ , ledit précurseur de complexe métalloïde-ligand est  $Si[N(CH_3)_2]_4$ , ladite première température est de 280°C et ladite seconde température distincte est de 430°C.
  11. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel ledit mélange est mélangé avec une source d'oxygène avant de déposer ladite couche de plusieurs composés métalliques sur ledit substrat, dans lequel ledit précurseur de complexe métal-ligand est le t-butyl $N=Ta[N(CH_2CH_3)_2]_3$ , ledit précurseur de complexe métalloïde-ligand est  $Si[N(CH_3)_2]_4$ , ladite première température est de 300°C et ladite seconde température distincte est de 435°C.
  12. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel ledit mélange est mélangé avec une source d'azote avant de déposer ladite couche de plusieurs composés métalliques sur ledit substrat, dans lequel ledit précurseur de complexe métal-ligand est  $Zr[N(CH_2CH_3)_2]_4$ , ledit précurseur de complexe métalloïde-ligand est  $Si[N(CH_3)_2]_4$ , ladite première température est de 300°C et ladite seconde température distincte est de 360°C.
  13. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel ledit mélange est mélangé avec une source d'azote avant de déposer ladite couche de plusieurs composés métalliques sur ledit substrat, dans lequel ledit précurseur de complexe métal-ligand est le t-butyl $N=Ta[N(CH_2CH_3)_2]_3$ , ledit précurseur de complexe métalloïde-ligand est  $Si[N(CH_3)_2]_4$ , ladite première température est de 310°C et ladite seconde température distincte est de 350°C.



FIG. 1

